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Spectroscopic Evidence for the Existence of Two Discrete Dodecahedral Configurations for the Octacyanoniobate(IV) Ion

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Salts of the [$Nb(CN)_8$]$^{4-}$ ion have been studied at room temperature in magnetically dilute powders by electron paramagnetic resonance spectroscopy. The spectra indicate two distinct configurations, each classifiable as dodecahedral. The relationship of these two structures to crystallographically known octacyano configurations is briefly discussed, and a new interpretation of the e.p.r. spectra of the [$Nb(CN)_8$]$^{4-}$ ion in frozen solutions is also suggested.

Introduction

It has long been known that the configuration of an eight-coordinate species can be critically sensitive to its physical environment. Most evidence concerns configurational changes upon solution, although both the [$Mo(CN)_8$]$^{4-}$ [1, 2] and [$Mo(CN)_8$]$^{3-}$ [3, 4] ions have been found by crystallographic and spectroscopic techniques to have at least two solid state configurations, one dodecahedral and one square antiprismatic. The previous use of e.p.r. for solid state studies on octacyano systems [3, 5, 6] has generally (and necessarily) entailed the use of either undiluted solids or stoichiometrically non-equivalent host lattices, however, and whereas the former method can yield only limited information, the latter may impose such harsh constraints on the paramagnetic species that its configuration may be substantially different from its preferred (pure solid) geometry. Such behaviour has indeed been purported to occur for the potassium salts of the [$M(CN)_8$]$^{3-}$ ions (M = Mo, W) [4].

The recently reported octacyanoniobate(IV) ion [7], however, provides an excellent opportunity to observe an octacoordinate anion in a variety of crystal packings, since, by the use of salts of the stoichiometrically equivalent, diamagnetic [$Mo(CN)_8$]$^{4-}$ ion, it is possible to study by e.p.r. [$Nb(CN)_8$]$^{4-}$ salts in environments which approach the ideal of an isomorphous host lattice.

Experimental

The tetracaesium (dihydrate) and tetrasodium (tetrahydrate) [$Nb(CN)_8$]$^{4-}$ salts were prepared by their literature methods [4]. The tetrakis(tetramethylammonium) and tetrakis(tetraethylammonium) salts were prepared by decomposition of the tetrathallium (I) salt with the appropriate tetraalkylammonium chloride. Analogous [$Mo(CN)_8$]$^{4-}$ salts were made from its tetrasilver(I) salt by similar procedures. Carbon, hydrogen and nitrogen analyses were obtained to support all formulae.

Approximately 1/2% solid solutions were obtained for e.p.r. study by rapid precipitation from solutions containing the niobate and appropriate molybdate salts.

E.p.r. spectra were measured on a Varian E-12 X-band spectrometer, with 100 kHz modulation; infrared spectra on a Perkin–Elmer 325 spectrophotometer over the range 200–2200 cm^{-1}, using nujol mulls; and Raman spectra on a Cary 81 instrument with a CRL 52MG laser (argon–krypton) using 6471 Å excitation.

Results and Discussion

The e.p.r. spectra of the [$Nb(CN)_8$]$^{4-}$ salts may be interpreted in terms of two basic, discrete configurations (X, Y). The reported spectra[4] of the potassium and di-n-propylammonium salts are almost identical, giving values of $g_\perp \gg g_\parallel$ and $A_\parallel \gg A_\perp$, as expected for a dodecahedral geometry. It is thus likely [4] that these two salts contain anions with a dodecahedral configuration (X) related to that of the molybdate isomorph of the potassium salt [1].

For the spectra of the tetraalkylammonium salts, however, we find that, although $g_\perp > g_\parallel$ and $A_\parallel > A_\perp$ still, the differences are very much smaller, with both components of the g and A tensors being of comparable magnitude (Fig. 1, Table I). This seems to indicate a quite different distortion (Y) from dodecahedral (D_{2d}) symmetry. The spectrum of the caesium salt is characteristic of a Y configuration that has suffered a further minor distortion, resulting in loss of axial symmetry and resolution of separate g_x,

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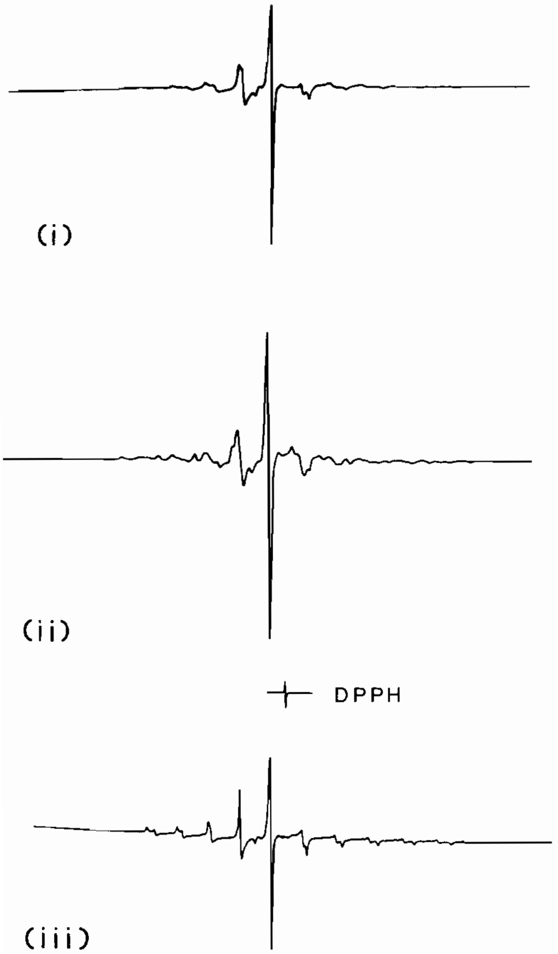

Fig. 1. E.p.r. spectra of Y-type octacyanoniobates(IV). (i) $\{(CH_3)_4N\}_4[Nb(CN)_8]$, (ii) $Cs_4[Nb(CN)_8]\cdot 2H_2O$, (iii) $Na_4[Nb(CN)_8]\cdot 4H_2O$.

g_y, and g_z features. The sodium salt gives a spectrum that may be considered as two Y-type spectra superimposed, suggesting the existence of two slightly differing environments for the anion. That the relative intensities of these two sets are seen to vary over a period of days is in keeping with the pure salt's tendency to effloresce (an effect also noted for $Na_3[W(CN)_8]\cdot 4H_2O$ [8]). Such behaviour may yield a lattice wherein the paramagnetic ions are packed in proximity to a variable number of water molecules.

Thus, for the first time, e.p.r. can be seen to distinguish between two substantially different dodecahedral configurations for an octacyano species. It is also apparent that, apart from minimal deviations, no salt has been found to possess a structure truly intermediate between X and Y, and evidently these configurations represent discrete energy minima. Although no evidence has been found for a square antiprismatic (D_{4d}) configuration for any of the $[Nb(CN)_8]^{4-}$ salts, that considerable mixing of d_{z^2} character into the d_{xy} ground state of the Y-type dodecahedron occurs (in other words, a distortion towards the D_{4d} geometry) is indicated by the closeness of the anisotropic components of the g and A tensors. Indeed, were it not for the resolving effect of the hyperfine splitting, a practically symmetric signal, such as those found for $[(C_4H_9)_4N]_3$-$[W(CN)_8]$ [6] and $[(C_4H_9)_4N]_3[Mo(CN)_8]$ [3], would probably be observed. The Y-type spectra may thus even represent the D_2 configuration found for this molybdate salt [3].

The vibrational spectra of the niobate salts support, to a certain extent, the distinction between the X and Y configurations. In the sensitive cyanide-stretching region, the Y-type salts (Table II) generally give a single infrared band with a number of poorly resolved shoulders, while the X-type spectra are much better resolved, with a broader spread of frequencies.

These results lead to an alternative explanation of the e.p.r. spectrum of the octacyanoniobate(IV) ion in frozen solutions [4] as an unresolved Y-type spectrum with the anisotropic g and A parameters differing insufficiently for resolution of the solvent-broadened spectrum. This may be reconciled to the observed $\langle g \rangle$ and $\langle A \rangle$ values at room temperature by considering a configurational change on cooling. The measured $\langle g \rangle$ and $\langle A \rangle$ values are consistent with an X geometry persisting in solution at room temperature, and, since both X and Y represent distortions

TABLE I. E.p.r. Data for Octacyanoniobates(IV).

	$g_\parallel$	$g_\perp$	$\langle g \rangle^a$	$A_\parallel$ (cm^{-1} × 10^4)	$A_\perp$	$\langle A \rangle^a$
$K_4[Nb(CN)_8]\cdot 2H_2O^b$	1.972	1.990	1.984	152	73	99
$\{(C_3H_7)_2NH_2\}_4[Nb(CN)_8]^b$	1.969	1.991	1.984	147	74	98
$\{(CH_3)_4N\}_4[Nb(CN)_8]$	1.965	1.969	1.968	128	100	109
$\{(C_2H_5)_4N\}_4[Nb(CN)_8]$	1.962	1.964	1.963	126	106	113
$Cs_4[Nb(CN)_8]\cdot 2H_2O$	1.958	1.958 1.959	1.958	137	118 107	121
$Na_4[Nb(CN)_8]\cdot 4H_2O$	1.962 1.964	1.966 1.968	1.965 1.967	122 131	112 105	115 114

[a] Calculated from perpendicular and parallel planes. [b] Ref. 4.

TABLE II. Vibrational Data for Octacyanoniobates(IV).

		ν(CN)	ν(MC), δ(MCN), or δ(CMC)[a]
$K_4[Nb(CN)_8]\cdot 2H_2O$[b]	R	2138(3), 2131(8), 2123(10), 2096(3), 2074(1)	496(2), 450(5), 427(6), 397(4), 362(6), 345(2), 320(1), 301(2), 278(6), 241(1)
	IR	2136s, 2129s, 2123s, 2114vs, 2070w, 2027w	498b, 471s, 439s, 377sh, 342vs
$\{(C_3H_7)_2NH_2\}_4[Nb(CN)_8]$[b]	R	2129(10), 2124(8), 2112(5), 2093(4)	528(1), 443(2), 417(4), 399(3), 319(10), 292(7), 268(3), 243(3)
	IR	2145w, 2124m, 2119s, 2115m, 2103s, 2102sh, 2090s	450m, 432w, 414vw, 370m, 341s, 300vw
$\{(CH_3)_4N\}_4[Nb(CN)_8]$	R	2129(9), 2123(10), 2119(9)	488(1), 459(4), 427(7), 411(6), 373(6), 312(1), 296(6)
	IR	2133m, sh, 2125s, sh, 2117vs	452m, 428w, 339s
$\{(C_2H_5)_4N\}_4[Nb(CN)_8]$	R	2122(5), 2114(10), 2106(5)	489(1), 471(4), 420?, 404?, 340(4), 291(6)
	IR	2125m, sh, 2118vs	445m, 422w, 340s
Cs4			
$Cs_4[Nb(CN)_8]\cdot 2H_2O$	R	2143(1), 2139(1), 2134(3), 2123(10), 2119(5), 2111(3)	488(2), 430(6), 352(3), 294(3)
	IR	2116s, sh, 2113vs, 2108s, sh, 2071w	560b, 452m, 428w, 338s
$Na_4[Nb(CN)_8]\cdot 4H_2O$	R	2138(10), 2127(6), 2122(4), 2118(2)	488(1), 464(2), 435(7), 417(6), 360(4), 310(4), 300(6)
	IR	2145m, 2137m, 2134m, 2127vs, 2124s 2118m	540m, b, 483w, 457m, 435w, 382w, 346s, 302vw

[a] Absorptions due to cations not included. [b] Ref. 4.

of a dodecahedron, there would undoubtedly be only a very small energy barrier to interconversion. Temperature variation studies were found unable, however, to decide between this explanation and the previous proposal [4] of conversion to square antiprismatic geometry (in a further study, the spectra of the dilute powders were found to remain essentially unchanged over the range 100–295 K).

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